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(54) THE PREPARATION OF 2,2-DIMETHYL-3-(2',2'-DICHLOROVINYL)-CYCLOPROPANE-1-CARBOXYLIC ACID

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate, organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

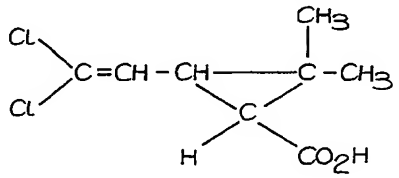
The present invention relates to an unobvious process for the preparation of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid, which is used as an intermediate for the preparation of valuable insecticides (see DOS (German Published Specifications) 2,326,077, 2,418,950, 2,436,178 and 2,439,177).

A simple and economical synthesis of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid has not been disclosed hitherto. A synthesis route which is known from the literature (Chemical Abstracts *52*, 13,650 and Coll. Czech, Chem. Comm. *24*, 2,230, 1959) requires, for example, a reaction with ethyl diazoacetate, which is explosive, toxic and not very stable on storage. Moreover, the yields from this reaction are unsatisfactory.

Another synthesis (see DOS (German Published Specifications) 2,326,077 and 2,439,177) starts from caronaldehyde which is accessible only with difficulty and is obtained by ozonolysis of chrysanthemic acid ester. Ozone is explosive and its preparation entails high energy costs. The end stage is obtained by a Wittig reaction which is expensive and technically can be carried out only with difficulty (working under nitrogen). In addition, the yields obtained from this synthesis route are on the whole unsatisfactory.

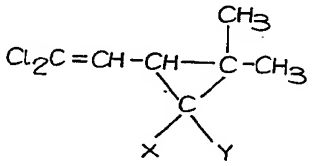
There was thus a need to develop a synthesis of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid which can be carried out technically even on a relatively large scale and which proceeds with good yields.

The present invention now provides a process for the preparation of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid



(I)

in which (a) a 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropanecarboxylic acid derivative of the general formula



(II)

in which

X and Y, which can be identical or different, each represent CN or the radical —COOR,

in which

R represents C_1—C_4 alkyl or represents aralkyl or aryl, is completely or partially saponified in the presence of a base and the resulting 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid, or the dicarboxylic acid monoester or the 1 - cyano - cyclopropane - 1 - carboxylic acid, is decarboxylated at a temperature of from 80 to 230°C in the pressure of a base, or

(b) a 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - carboxylic acid derivative of the general formula (II) above,

in which

Y represents the radical —COOR

in which

R has the above-mentioned meaning, and

X represents the radical —COR^1,

in which

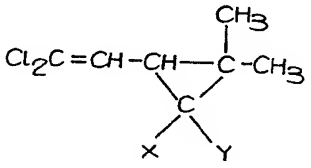
R^1 represents C_1—C_4 alkyl, is subjected, in the presence of a base, to elimination of the alkylcarbonyl radical (—COR^1) and saponification of the remaining ester grouping, or

(c) a 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - carboxylic acid derivative of the general formula (II) above,

in which

X and Y each represent the radical —$COCH_3$, is subjected, in the presence of a base, to elimination of the acetyl radical (—$COCH_3$) and the resulting ketone is oxidised.

The 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - carboxylic acid derivatives of the general formula



(II)

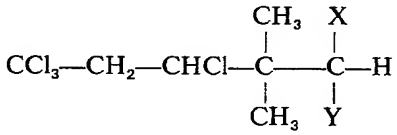
in which

X and Y, which may be identical or different, each represent CN, the radical —COOR or the alkylcarbonyl radical —COR^1,

in which

R represents C_1—C_4 alkyl, aralkyl or aryl and

R^1 represents C_1—C_4 alkyl, which can be used as starting materials in these processes, are new and can be obtained by reacting a compound of the general formula

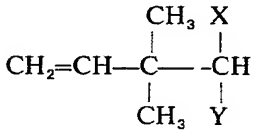


(III),

in which

X and Y have the above-mentioned meanings, with a strong base in the presence of a diluent.

The compounds of the formula (III) are new and can be obtained by reacting a compound of the general formula



(IV),

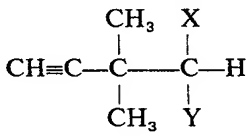
in which

X and Y have the above-mentioned meanings, with CCl_4 in the presence of a

diluent and of a suitable catalyst. (See U.K. Patent Application 39954/77, Serial No. 1,571,433).

The compounds of the formula (IV) are new and can be obtained by

(a) hydrogenating a compound of the general formula

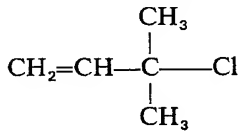


(V)

in which

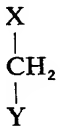
X and Y have the above-mentioned meanings, with hydrogen in the presence of a Lindlar catalyst, or by

(b) reacting 3 - methyl - 3 - chloro - but - 1 - ene of the formula



(VI)

with a compound of the general formula



(VII),

in which

X and Y have the above-mentioned meanings, in the presence of a basic catalyst and/or a diluent. (See U.K. Patent Application No. 39955/77. Serial No. 1,571,434.

3 - Methyl - 3 - chloro - but - 1 - ene is known (see J. Chem. Soc. London 1948, page 530).

The compounds of the formula (VII) are known or can be prepared analogously to known processes.

The compounds of the formula (V) are known or can be prepared analogously to known processes (see J. Biol. Chem., volume 175, page 771; 1948).

Preferred starting compounds of the formula (V) and (VII) are those in which X and Y are identical or different and represent CN, acetyl ($-COCH_3$) or the radical —COOR in which R represents C_{1-4}-alkyl, benzyl or phenyl.

Compounds in which X and Y represent an alkoxycarbonyl group —COOR, in which R represents methyl, ethyl or tert.- butyl, are particularly preferred.

The compounds of the formula (IV) are obtained from the starting materials of the formula (V) by a reaction which is in itself known, that is to say the partial reduction of alkynes with hydrogen in the presence of so-called Lindlar catalysts, or by reacting 3 - methyl - 3 - chlorobut - 1 - ene with compounds of the formula (VII) in the presence of basic agents.

Basic agents which can be used are, for example, alkali metal hydroxides, such as NaOH or KOH, carbonates, such as Na_2CO_3 or K_2CO_3, or, preferably, alcoholates, such as sodium methylate, sodium ethylate, sodium isopropylate or potassium tert.-butylate. In the latter case, the solvents used are preferably alcohols, such as methanol, ethanol, isopropanol or butanol.

Other solvents which can be used are: hydrocarbons, such as pentane, hexane or toluene, ethers, such as tetrahydrofuran, dioxan, diisopropyl ether or glycol dimethyl ether, or ketones, such as acetone or butanone.

The reaction is carried out at temperatures between 0° and 150°C, and preferably between 20°C and 100°C.

Compounds of the formula (III) are prepared by an addition reaction of carbon tetrachloride with compounds of the formula (IV).

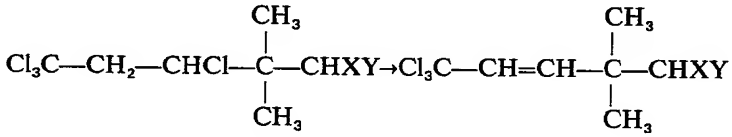
An addition reaction of carbon tetrachloride with olefins is known. It is catalysed by compounds which form free radicals, such as, for example, peroxides or azo compounds, or by transition metal complexes or by catalyst systems which contain copper (I) salts and a base, for example piperidine.

The addition reaction is preferably carried out in the presence of a peroxide, such as, for example, di-tert.-butyl peroxide or benzoyl peroxide, or of an azo compound, such as, for example, azo-bis-isobutyronitrile; benzoyl peroxide is particularly preferred.

The reaction is usually carried out using carbon tetrachloride as the solvent and can be carried out under normal pressure or elevated pressure. The temperature range accordingly extends from 77° up to 150°C. However, the reaction can also be carried out in other inert organic solvents.

The conversion of compounds of the formula (III) to compounds of the formula (II) proceeds surprisingly smoothly and with good yields in a single stage. Inasmuch as cyclopropane ring closures of this type which are known from the literature are carried out virtually exclusively with bromine compounds which are very much more reactive, this was not to be expected.

The elimination of hydrogen chloride to give the dichlorovinyl group, which proceeds at the same time and with good yields, is particularly unusual and was not to be expected by those skilled in the art. As a rule, an elimination of this type does not proceed without problems and gives poor yields. Thus, for example, it had to be expected that one or more chlorine atoms would be replaced nucleophilically by the corresponding radical of the base, for example by a methoxy or ethoxy group. Thus, for example, elimination of hydrogen chloride from the trichloromethyl group of 1,1,1,3-tetrachloro-4-methylpentane cannot be carried out at all (Coll. Czech. Comm. *24*, page 2,231 and 2,232, 1959). Moreover, an elimination of hydrogen chloride in accordance with the following reaction equation had to be expected.



The conversion of compounds of the formula (III) to compounds of the formula (II) can be carried out with strong bases, such as, for example, NaOH or KOH, or alcoholates, such as sodium methylate, sodium isopropylate or potassium tert.-butylate. The procedure is preferably such that the compounds of the formula (III) are added to a solution containing the base, the addition being made for example initially at from 0° to 40°C and preferably at 10° to 25°C and the mixture then being heated for example to from 50° to 150°C, and preferably 65° to 120°C, until the reaction has ended.

Solvents which can be used are, for example, hydrocarbons, ethers and, preferably, alcohols, such as, for example, methanol, ethanol, propanol, isopropanol, butanol, tert.-butanol, glycol, glycol monomethyl ether or glycol monoethyl ether.

When alkali metal hydroxides are used as the basic agent, the reaction is preferably carried out in a two-phase system—such as, for example, toluene/water—and a catalyst, such as, for example, tertiary amines or quaternary ammonium or phosphonium salts, is appropriately added.

Sodium methylate or sodium ethylate is preferably used for the conversion of compounds of the formula (III) to compounds of the formula (II).

The following compounds of the formula (II) are preferably used for the preparation of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid of the formula (I):

1) 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid dimethyl ester,

2) 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid diethyl ester,

3) 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid ethyl - tert. - butyl ester,

4) 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - acetyl - 1 - carboxylic acid ethyl ester,

5) 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - cyano - 1 - carboxylic acid ethyl ester,

6) 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - cyano - 1 - carboxylic acid butyl ester,

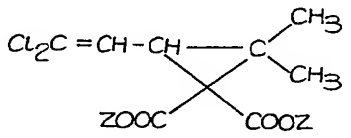
7) 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - acetyl - 1 - carboxylic acid tert.-butyl ester, and

8) 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - 1,1 - diacetyl - cyclopropane.

The mode of preparation of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid from the compounds of the formula (II) differs somewhat depending on the meaning of the radicals X and Y.

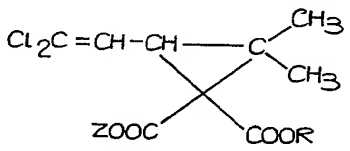
1) X and Y represent alkoxycarbonyl (—COOR).

Saponification and decarboxylation are carried out. Starting materials for the decarboxylation are 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid, or its salts, of the general formula



in which

Z denotes a hydrogen atom or an equivalent of a metal atom, such as, for example, Li, Na, K or ½Ca, but the two Z's do not both denote hydrogen at the same time, or the 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid monoesters, or their salts, of the general formula



in which

Z and R have the above-mentioned meaning.

Such a partial or complete saponification of compounds which are analogous to malonates is known in principle and can be carried out in accordance with methods known from the literature (see J. Am. Chem. Soc. volume *66*, page 1,287 (1944) and Organikum (Organic Chemistry), VEB Deutscher Verlag der Wissenschaften, Berlin 1972, 11th Edition, pages 457 and 458). Saponification to the half-ester is usually carried out at room temperature.

The decarboxylation can be carried out with or without solvents but a solvent is preferably used.

Solvents which can be used are alcohols, such as, for example, ethylene glycol, diethylene glycol or triethylene glycol; dimethylsulphoxide (DMSO), hexamethylphosphoric acid triamide (HMPT) or sulpholane; ethers, such as, for example, diethylene glycol diethyl ether or diethylene glycol dibutyl ether; hydrocarbons, such as, for example, decahydronaphthalene or tetrahydronaphthalene; and heterocyclic bases, such as, for example, pyridine and methylsubstituted pyridines, such as, for example, collidine, or quinoline and quinolines substituted by methyl groups, such as, for example, lepidine, quinaldine or 2,4-dimethylquinoline, and also cyclic amidines, such as, for example, 1,5 - diazo - bicyclo[4.3.0]non - 5 - ene (DBN) or 1,8 - diaza - bicyclo - [5.4.0]undec - 7 - ene (DBU), or amides, such as, for example, pyrrolidone, 1-methyl-pyrrolidone, ε-caprolactam or 1-methyl caprolactam.

If the reaction is not carried out in a basic solvent it is necessary to add a base. Bases which can be used are amines, alkali metal hydroxides or carbonates and alkaline earth metal hydroxides or carbonates. Furthermore, in the case of decarboxylation reactions, acceleration of the reaction is frequently achieved by the addition of copper powder or copper (I) salts.

The decarboxylation can be carried out at temperatures between 100° and 230°C and preferably at from 150° to 200°C.

The reaction can be carried out under normal pressure, under reduced pressure or at elevated pressure.

2) X represents alkylcarbonyl (—COR^1) and Y represents alkoxycarbonyl (—COOR).

Scission is effected with strongly basic agents. By this means, elimination of the alkylcarbonyl group is achieved and esters of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl - cyclopropane - 1 - carboxylic acid, of the formula (I), are obtained and these can be saponified by routes which are known from the literature (see, for

example, Coll. Czech. Chem. Comm. *24*, 2,234; 1959) to give the free acid. In order to prevent side reactions during the elimination of the alkylcarbonyl group, esters which are difficult to saponify under alkaline conditions and in which R represents, for example, isopropyl or tert.-butyl, are preferably employed.

Strong bases that are preferably employed are KOH or NaOH and the reaction mixture is then preferably heated to 80°—120°C, using a solvent. Solvents which can be used are, in particular, water and aqueous or non-aqueous alcohols.

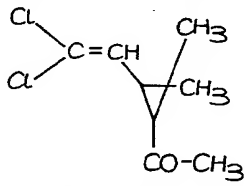
3) X represents CN and Y represents alkoxycarbonyl (—COOR).

In principle, the conversion proceeds as described under 1) above, but the decarboxylation proceeds at lower temperatures, preferably from 120 to 200°C.

4) X and Y represent acetyl.

In this case also an acetyl group can be eliminated successfully by methods known from the literature.

The acid (I) is obtained by oxidising the ketone of the formula



which has formed as a result of the elimination, with a hypobromite or hypochlorite solution.

The process of this invention is illustrated by the following Examples, which also illustrate the preparation of certain starting materials for use in accordance with the invention.

Example 1

113 g of dimethylpropynyl-malonic acid diethyl ester were dissolved in 500 ml of petroleum ether in a hydrogenation autoclave with a glass insert, 10 g of a Lindlar catalyst (5% Pd on $CaCO_3$) were added and the hydrogenation was carried out at 70°C until the theoretically calculated amount of hydrogen had been taken up. The mixture was then allowed to cool, the catalyst was filtered off and the solvent was stripped off under reduced pressure. 108 g of a very slightly yellowish coloured liquid remained and according to analysis by gas chromatography this consisted to the extent of 90% of 1,1-dimethyl-2-propenylmalonic acid diethyl ester. Yield: 86% of theory. The nuclear magnetic resonance spectrum confirmed the structure: δ (in $CDCl_3$): 1.2 ppm (singlet+triplet, 12 protons); 3.3 ppm (singlet, 1 proton); 4.15 ppm (quartet, 4 protons); and 4.95 ppm and 6 ppm (multiplet; 2+1 protons).

Example 2

250 g of crude dimethyl-propenyl-malonic acid diethyl ester (approximately 90% pure) were dissolved in 2,000 ml of dry carbon tetrachloride and 40 g of benzoyl peroxide were added. The mixture was boiled for 8 hours under reflux 20 g of benzoyl perioxide were added and the mixture was boiled for a further 8 hours. After cooling, the mixture was washed with cold dilute sodium hydroxide solution in order to remove the benzoic acid formed and the organic phase was dried with sodium sulphate and filtered and the solvent was distilled off under reduced pressure. The residue was subjected to fractional distillation under a high vacuum. 277 g of 1,1 - dimethyl - 2,4,4,4 - tetrachlorobutyl - malonic acid diethyl ester with a boiling point of 132—138°C/0.2 mm Hg were obtained. Yield: 73% of theory. The nuclear magnetic resonance spectrum confirmed the structure: δ (in $CDCl_3$): 1.35 ppm (multiplet, 12 protons); 3.2 ppm (multiplet, 2 protons); 3.9 ppm (singlet, 1 proton); 4.25 ppm (quartet, 4 protons); and 4.8 ppm (multiplet, 1 proton).

Example 3

25 g of sodium were dissolved in 2,000 ml of absolute ethanol, 181 g of 1,1 - dimethyl - 2,4,4,4 - tetrachlorobutyl - malonic acid diethyl ester were added dropwise at room temperature and after the dropwise addition was complete the mixture was heated for 4 hours under reflux. It was allowed to cool and filtered, the solvent was distilled off under reduced pressure and the residue was rendered acid with ice-cold dilute hydrochloric acid. After extracting three times with methylene

chloride, the combined organic phases were washed with potassium carbonate solution and then with water and dried over sodium sulphate. The mixture was filtered, the solvent was stripped off *in vacuo* and the residue was distilled under a high vacuum. 115 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid diethyl ester with a boiling point of 102—105°C/0.1 mm Hg were obtained. The nuclear magnetic resonance spectrum confirmed the structure: δ ($CDCl_3$): 1.3 ppm (multiplet, 12 protons); 2.55 ppm (doublet, 1 proton); 4.25 ppm (quartet, 4 protons) and 5.9 ppm (doublet, 1 proton). The refractive index n_{20}^{D} was 1.4830.

Example 4

21 g of KOH in 50 ml of water, 100 ml of ethanol and 30.9 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid diethyl ester were heated for 4 hours under reflux. After cooling, the mixture was extracted twice with methylene chloride and the aqueous phase was acidified with hydrochloric acid, whilst cooling with ice, and extracted five times with methylene chloride. The methylene chloride phase was washed with a saturated solution of sodium chloride and then with water, dried over sodium sulphate and filtered and the methylene chloride was stripped off *in vacuo*. When the residue was left to stand, 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid crystallised and this could be recrystallised from chloroform/petroleum ether. Melting point: 138—140°C. The nuclear magnetic resonance spectrum confirmed the structure: δ (d_6-acetone): 1.3 ppm (singlet, 6 protons); 2.55 ppm (doublet, 1 proton); 6.1 ppm (doublet, 1 proton) and 10.4 ppm (singlet, 2 protons).

Example 5

2.53 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid were dissolved in 50 ml of ethanol, whilst stirring, and 100 ml of 0.1 N NaOH were added. The solvents were stripped off under reduced pressure and the dried residue was suspended in 25 ml of quinoline. After adding 100 mg of copper powder the mixture was heated to about 160—170°C for 5 hours. After cooling, the mixture was rendered acid with ice-cold dilute hydrochloric acid and extracted five times with methylene chloride. After the organic phase had been dried over sodium sulphate, the mixture was filtered and the filtrate was evaporated in a rotary evaporator and a few millilitres of petroleum ether were added to the residue. The mixture crystallised after standing for some time. 1.3 g of 2,2 - dimethyl - 3 - (2,2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid (cis/trans mixture) with a melting point of 67—70°C were obtained.

Example 6

23 g of sodium were dissolved in 500 ml of absolute ethanol, 176 g of malonic acid diethyl ester were added dropwise, 1 g of hydroquinone was added and 104.5 g of 3 - chloro - 3 - methyl - 1 - butene (prepared according to J. Chem. Soc. London *1948*, page 530) were then added dropwise at 60—70°C. When the dropwise addition was complete, the mixture was heated to the reflux temperature for a further one hour. It was then allowed to cool and left to stand overnight. After filtering, the sodium chloride which had been filtered off was rinsed with ethanol and the combined filtrates were concentrated *in vacuo*. The residue was rendered acid with ice-cold dilute hydrochloric acid and extracted three times with methylene chloride. The methylene chloride extracts were washed with sodium carbonate solution and then with water, the organic phase was dried over sodium sulphate, the mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was subjected to fractional distillation. 161 g of a liquid which had a boiling point of 76—82°C/0.2 mm Hg were obtained. As was found by analysis by gas chromatography, the product was identical with the 1,1-dimethyl-propenylmalonate obtained in Example 1.

Example 7

2.53 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid were suspended in 50 ml of water. 200 ml of 0.1 N potassium hydroxide solution were added and the mixture was stirred until all the solids had dissolved. The water was removed carefully *in vacuo* and the dried residue was suspended in 50 ml of ethylene glycol; 1 ml of DBU was added and the mixture was

heated to the reflux temperature for 8 hours. After cooling, 150 ml of water was added and the mixture was extracted five times by shaking with methylene chloride. The methylene chloride extracts were discarded. The aqueous phase was then acidified with ice-cold dilute hydrochloric acid and again extracted five times with methylene chloride. The combined methylene chloride extracts were dried over sodium sulphate. After filtering and concentrating *in vacuo*, a little ice-cold petroleum ether was added and the mixture was left to stand. 1.5 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid (cis/trans mixture) which had a melting point of 64—66°C were obtained.

Example 8

30.9 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid diethyl ester were dissolved in 65 ml of ethanol. A solution of 5.6 g of potassium hydroxide in 65 ml of absolute ethanol was added dropwise to this solution in the course of one hour. The mixture was stirred for a further 10 hours and left to stand overnight. The solution developed a dark coloration. It was heated to the boil and filtered hot. The solution was concentrated somewhat *in vacuo*, cooled at 0°C and filtered. The material on the filter was dissolved in 50 ml of water and the mixture was carefully rendered acid with hydrochloric acid, whilst cooling with ice. It was then extracted three times with methylene chloride and the extracts were dried over sodium sulphate and filtered and the solvent was removed *in vacuo*. The residual oil displayed a nuclear magnetic resonance spectrum which agreed with the structure of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid monoethyl ester: δ (d_6-acetone); 1.3 ppm (multiplet, 9 protons); 2.55 ppm (doublet, 1 proton); 4.25 ppm (quartet, 2 protons); 6.05 ppm (doublet, 1 proton) and 10.1 ppm (singlet, proton).

Example 9

14.05 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid monoethyl ester were dissolved in 100 ml of 2,4-dimethylquinoline, 1 g of copper powder was added and the mixture was heated to about 170°C for 5 hours. After cooling, 300 ml of water were added and the mixture was extracted with methylene chloride; the methylene chloride extracts were washed with dilute hydrochloric acid, then with an aqueous bicarbonate solution and then with water until neutral, dried over sodium sulphate and filtered and the methylene chloride was removed *in vacuo*. The residue was subjected to fractional distillation under a high vacuum. 7.8 g of an oil with a boiling piont of 64—78°/0.2 mm Hg were obtained and this was purified by a second distillation. Boiling point was 70—71°C/0.2 mm Hg. The nuclear magnetic resonance spectrum confirmed the structure of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl - cyclopropane - 1 - carboxylic acid ethyl ester (cis/trans mixture). The free acid could be obtained from 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid ethyl ester by the method according to Coll. Czech. Chem. Comm. *24*, 2,234.

Example 10

23 g of sodium were dissolved in 500 ml of absolute ethanol, 124 g of cyanoacetic acid ethyl ester were added dropwise and 102.5 g of 3 - chloro - 3 - methyl - 1 - butyne (prepared according to J. Am. Chem. Soc. *79*, 2,142; 1957) were then added dropwise at 60—70°C. When the dropwise addition was complete, the mixture was heated to the reflux temperature for a further one hour. After cooling, it was evaporated in a rotary evaporator and the residue was rendered acid with ice-cold dilute hydrochloric acid and extracted three times with methylene chloride. The methylene chloride extracts were washed with sodium carbonate solution and then with water and the organic phase was dried over sodium sulphate, filtered and concentrated under reduced pressure. The residue was subjected to fractional distillation under a high vacuum. 1,1 - Dimethyl - 2 - propynyl - cyanoacetic acid ethyl ester boiled at a boiling point of 92—98°C/0.5 mm Hg. The nuclear magnetic resonance spectrum confirmed the structure: δ (in $CDCl_3$): 1.3 ppm (triplet, 3 protons); 1.5 ppm (singlet, 6 protons); 2.4 ppm (singlet, 1 proton); 3.6 ppm (singlet, 1 proton) and 4.3 ppm (quartet, 2 protons).

Example 11

89.5 g of dimethyl-propynyl-cyanoacetic acid ethyl ester were dissolved in 500 ml of petroleum ether in a hydrogenation autoclave with a glass insert, 10 g of

Lindlar catalyst (5% Pd on $CaCO_3$) were added and the hydrogenation was carried out at 60—80°C until the theoretically calculated amount of hydrogen had been taken up. After cooling, the catalyst was filtered off and the solvent was removed under reduced pressure. 81 g of a yellow oil which consisted mainly of 1,1 - dimethyl - 2 - propenyl - cyanoacetic acid ethyl ester remained and this was employed directly in the next stage.

Example 12

81 g of crude 1,1 - dimethyl - 2 - propenyl - cyanoacetic acid ethyl ester were dissolved in 750 ml of carbon tetrachloride, 40 g of benzoyl peroxide were added and the mixture was boiled under reflux for 24 hours. After cooling, it was washed with cold dilute sodium hydroxide solution in order to remove the benzoic acid formed, the organic phase was dried with sodium sulphate and, after the sodium sulphate had been filtered off, the solvent was distilled off. The residue was subjected to fractional distillation under a high vacuum. 92 g of 1,1 - dimethyl - 2,4,4,4 - tetrachlorobutyl - cyanoacetic acid ethyl ester with a boiling point of 122—130°C/0.1 mm Hg were obtained.

The nuclear magnetic resonance spectrum confirmed the structure: δ (in $CDCl_3$): 1.25 ppm (multiplet, 9 protons); 3.2 ppm (multiplet, 2 protons); 4.2 ppm (multiplet, 1+2=3 protons); and 4.9 ppm (multiplet, 1 proton).

Example 13

25 g of sodium were dissolved in 2,000 ml of ethanol, 162.5 g of 1,1 - dimethyl - 2,4,4,4 - tetrachloro - butyl - cyanoacetic acid ethyl ester were added dropwise in the course of one hour, at 20°C, and after the dropwise addition was complete the mixture was heated under reflux for a further 3 hours. After cooling, the solvent was stripped off under reduced pressure and the residue was rendered neutral with ice-cold dilute hydrochloric acid. After extracting three times with methylene chloride, the combined organic phases were dried over sodium sulphate. The sodium sulphate was filtered off and the solvent was removed from the filtrate *in vacuo* and the residue was distilled under a high vacuum. 92.5 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - 1 - cyano - cyclopropane - 1 - carboxylic acid ethyl ester with a boiling point of 116—122°C/0.3 mm Hg were obtained. The nuclear magnetic resonance spectrum confirmed the structure: δ (in $CDCl_3$): 1.3 ppm (multiplet, 9 protons); 2.65 ppm (doublet, 1 proton); 4.3 ppm (quartet, 2 protons) and 6.2 ppm (doublet, 1 proton).

Example 14

26.2 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - 1 - cyano - cyclopropane - 1 - carboxylic acid ethyl ester were dissolved in a solution of 5.6 g of potassium hydroxide in 50 ml of ethylene glycol and the mixture was heated for 3 hours under gentle reflux. After cooling, the mixture was diluted with 50 ml of water and extracted three times with ether and the ether phase was washed once with water and once with a saturated solution of sodium chloride, dried over sodium sulphate, filtered and evaporated in a rotary evaporator. The residue was added to a solution of 10 g of KOH in 80 ml of ethylene glycol. The mixture was heated to the boil for 8 hours and allowed to cool. It was then diluted with 80 ml of water and extracted three times with ether. The ether phase was discarded. The aqueous phase was then carefully acidified (pH 1), whilst cooling with ice, and extracted five times with methylene chloride. The methylene chloride phase was dried over Na_2SO_4, the sodium sulphate was filtered off and the solvent was evaporated in a rotary evaporator. The residual oil solidified after some time. Yield: 16.4 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid (cis/trans mixture) with a melting point of 63—68°C.

Example 15

23 g of sodium were dissolved in 500 ml of absolute ethanol, 174 g of acetoacetic acid tert.-butyl ester were added, 1 g of hydroquinone was added and 104.5 g of 3-chloro-3-methyl-1-butene were then added dropwise at 60°C. When the dropwise addition was complete, the mixture was heated to the reflux temperature for a further one hour. It was then allowed to cool and left to stand overnight. The sodium chloride which had precipitated was filtered off and washed with ethanol and the solvent was stripped off from the combined filtrates under reduced pressure. The residue was rendered neutral with ice-cold dilute

hydrochloric acid and extracted three times with methylene chloride. The methylene chloride extracts were dried over sodium sulphate, the sodium sulphate was filtered off and the filtrate was concentrated *in vacuo*. The residue was subjected to fractional distillation under a high vacuum. 1,1 - Dimethyl - 2 - propenyl - acetoacetic acid tert.-butyl ester boils at a boiling point of 62—66°C/0.08 mm Hg. The nuclear magnetic resonance spectrum confirmed the structure: δ (in $CDCl_3$): 1.05 ppm (singlet, 9 protons); 1.3 ppm (singlet, 6 protons); 2.2 ppm (singlet, 3 protons); 3.5 ppm (singlet, 1 proton) and 4.9 and 5.9 ppm (multiplet, 2+1=3 protons).

Example 16

113 g of 1,1 - dimethyl - 2 - propenyl - acetoacetic acid tert.-butyl ester were dissolved in 1,000 ml of carbon tetrachloride and 40 g of benzoyl peroxide were added. The mixture was boiled for 8 hours under reflux, 20 g of benzoxyl peroxide were added and the mixture was boiled for a further 8 hours. After cooling, it was washed with cold dilute sodium hydroxide solution in order to remove the benzoic acid formed and the organic phase was dried with sodium sulphate and filtered and the solvent was distilled off under reduced pressure. The residue was subjected to fractional distillation under a high vacuum. 1,1 - Dimethyl - 2,4,4,4 - tetra - chloro - butyl - acetoacetic acid tert.-butyl ester boiled at a boiling point of 138—145°C/0.1 mm Hg. Yield: 128 g. The nuclear magnetic resonance spectrum confirmed the structure: δ (in $CDCl_3$): 1.05 ppm (singlet, 9 protons); 1.3 ppm (singlet, 6 protons); 2.2 ppm (singlet, 3 protons); 3.2 ppm (multiplet, 2 protons; 3.75 ppm (singlet, 1 proton) and 4.8 ppm (multiplet, 1 proton).

Example 17

5 g of sodium were dissolved in 400 ml of absolute ethanol, 76 g of 1,1 - dimethyl - 2,4,4,4 - tetrachlorobutylacetoacetic acid tert.-butyl ester were added dropwise at 20—25°C and, after the dropwise addition was complete, the mixture was heated under reflux for 3—4 hours. It was allowed to cool and filtered and the ethanol was distilled *in vacuo*. The residue was rendered neutral with ice-cold dilute hydrochloric acid and extracted three times with methylene chloride. After washing with water, the extracts were dried over sodium sulphate and filtered and the methylene chloride was removed *in vacuo*. 59 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - 1 - acetyl - cyclopropane - 1 - carboxylic acid tert.-butyl ester with a boiling point of 96—105°C/0.1 mm Hg were obtained by distillation under a high vacuum. The nuclear magnetic resonance spectrum confirmed the structure: δ (in $CDCl_3$): 1.05 ppm (singlet, 9 protons); 1.3 ppm (singlet, 6 protons); 2.2 ppm (singlet, 3 protons; 2.5 ppm doublet, 1 proton) and 5.85 ppm (doublet, 1 proton).

Example 18

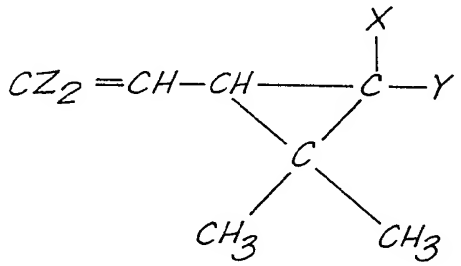
29.4 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - 1 - acetyl - cyclopropane - 1 - carboxylic acid tert.-butyl ester were mixed with a hot solution of 16.8 g of KOH in 12 g of water and the mixture was heated briefly (about 20 minutes) to the reflux temperature. After cooling, 300 ml of water were added and the pH of the mixture was adjusted to 8 with concentrated hydrochloric acid, whilst cooling with ice. The mixture was then extracted three times by shaking with methylene chloride and the extracts were washed with water until neutral, dried over sodium sulphate and filtered and the methylene chloride was removed *in vacuo*. After distillation under a high vacuum, 18 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid tert.-butyl ester (cis/trans mixture) with a boiling point of 84—93°C/0.4 mm Hg were obtained and this could be converted into the free acid by acid hydrolysis analogously to the instructions in Coll. Czech. Chem. Comm. *24*, 2,234.

Example 19

29.4 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - 1 - acetyl - cyclopropane - 1 - carboxylic acid tert.-butyl ester were mixed with a solution of 16.8 g of KOH in 20 ml of glycol monomethyl ether. After boiling under reflux for about one hour, the mixture was allowed to cool and 300 ml of water were added. The pH was adjusted to 8 with concentrated hydrochloric acid, whilst cooling with ice. The mixture was then extracted five times by shaking with methylene chloride. The subsequent working up can be seen from Example 18. 19.5 g of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid tert.-

butyl ester (cis/trans mixture) were obtained. This can be converted into the free acid by acid hydrolysis, as mentioned in Example 18.

We are aware of the complete specification of Patent No. 1,520,023 which describes and claims, inter alia, a compound of the formula:



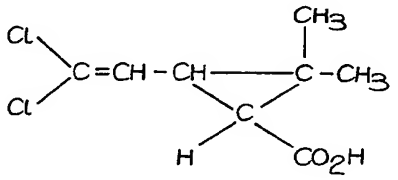
wherein X and Y are independently selected from cyano and alkoxy carbonyl containing from 1 to 4 carbon atoms in the alkoxy moiety, and Z is chlorine or bromine.

It is to be understood that we make no claim to a compound as claimed in the complete specification of Patent No. 1,520,023 as defined above.

Subject to the foregoing disclaimer

WHAT WE CLAIM IS:—

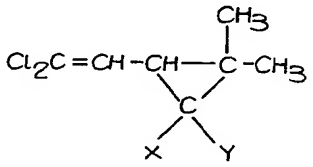
1. A process for the preparation of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid



(I),

in which

(a) a 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropanecarboxylic acid derivative of the general formula



(II),

in which

X and Y, which can be identical or different, each represent CN or the radical —COOR, but not X=Y=CN,

in which

R represents C_1—C_4 alkyl or represents aralkyl or aryl, is completely or partially saponified in the presence of a base and the resulting 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1,1 - dicarboxylic acid, or the dicarboxylic acid monoester, or the 1 - cyano - 1 - carboxylic acid, is decarboxylated at a temperature of from 80 to 230°C in the presence of a base or (b) a 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - carboxylic acid derivative of the general formula (II) above,

in which

Y represents the radical —COOR

in which

R has the above-mentioned meaning, and

X represents the radical —COR^1,

in which

R^1 represents C_1—C_4 alkyl, is subjected, in the presence of a base, to

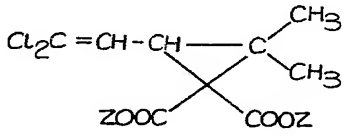
elimination of the alkylcarbonyl radical (—COR^1) and saponification of the ester grouping, or

(c) a 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - carboxylic acid derivative of the formula (II) above,

in which

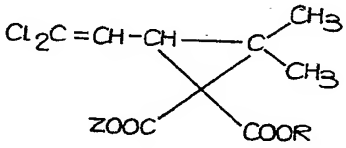
X and Y each represent the radical —$COCH_3$, is subjected, in the presence of a base, to elimination of an acetyl radical and the resulting ketone is oxidised.

2. A process according to claim 1(a), in which the product of the saponification stage has the general formula



in which

Z is a hydrogen atom or an equivalent of a metal atom, provided that both Z's are not hydrogen, or



in which

Z has the meaning stated above, and

R has the meaning stated in claim 1.

3. A process according to claim 2, in which Z is Li, Na, K or ½Ca.

4. A process according to claim 1(a), 2 or 3, in which the decarboxylation is effected in the presence of a solvent.

5. A process according to claim 4, in which the solvent is basic.

6. A process according to claim 1(a), 2, 3, or 4, in which the decarboxylation is effected in the presence of an amine as base.

7. A process according to claim 1(a), 2, 3, or 4 in which the base is an alkali metal hydroxide or carbonate, or an alkaline earth metal hydroxide or carbonate.

8. A process according to any of claims 1(a) and 2 to 7, in which the decarboxylation is effected in the presence of copper powder or of a copper (I) salt.

9. A process according to any of claims 1(a) and 2 to 8, in which the decarboxylation reaction is effected at between 100° and 230°C.

10. A process according to claim 9, in which the decarboxylation reaction is effected at between 150° to 200°C.

11. A process according to claim 1(b), in which R is isopropyl or tert.-butyl.

12. A process according to claim 1(b) or 11, in which the base is sodium or potassium hydroxide.

13. A process according to claim 1(b), 11 or 12, in which the reaction is effected at from 80° to 120°C.

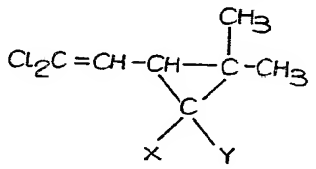
14. A process according to claim 1(b), 11, 12 or 13, in which the reaction is effected in the presence, as a solvent, of water, an alcohol or an aqueous alcohol.

15. A process according to claim 1(c) in which the ketone is oxidised by means of hypochlorite or hypobromite solution.

16. A process for the preparation of 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid, substantially as described in any one of Examples 5, 7, 14, 18 and 19.

17. 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - 1 - carboxylic acid whenever prepared by a process according to any of claims 1 to 16.

18. A process for the preparation of a 2,2 - dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropanecarboxylic acid derivative of the general formula



(II),

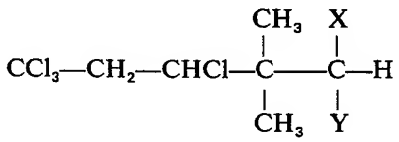
in which

X and Y, which may be identical or different, each represent CN, the radical —COOR or the radical —COR^1, but not X=Y=CN,

in which

R represents C_1—C_4 alkyl, aralkyl or aryl and

R^1 represents C_1—C_4 alkyl, in which a compound of the general formula

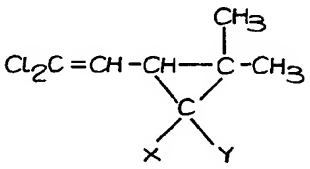


(III),

in which

X and Y have the above-mentioned meanings, is reacted with a strong base in the presence of a diluent.

19. 2,2 - Dimethyl - 3 - (2',2' - dichlorovinyl) - cyclopropane - carboxylic acid derivatives of the general formula



(II)

in which

X and Y, which may be identical or different, each represent CN, the radical —COOR or the radical —COR^1, but not X=Y=CN,

in which

R represents C_1—C_4 alkyl, aralkyl or aryl and

R^1 represents C_1—C_4 alkyl.

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